# Steam reforming of methane under water deficient conditions over gadolinium-doped ceria

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ABSTRACT

The catalytic properties of gadolinium-doped ceria (CGO) in methane steam reforming were studied. Catalytic tests were carried out between 750 and 900 °C, for $H_2O/CH_4$ ratios varying between 0.1 and 1, pretreated in $H_2O/N_2$, $N_2$ and $H_2/N_2$. Above 800 °C, slight deactivation with time on stream was observed except for the $H_2$-pretreated sample. Surface area measurements, $O_2$ adsorption at room temperature and $O_2$-temperature programmed oxidation experiments were performed after catalytic testing. Changes in both surface area and redox properties of CGO were observed and related to catalytic deactivation. Hydrogen is thought to play a key role in catalytic activity and deactivation process.

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## 1. Introduction

Among recent developments in Solid Oxide Fuel Cell (SOFC) technology, many studies concern the direct feeding of SOFCs with hydrocarbons from fossil or renewable sources. This strategy appears more attractive than the common technology based on using hydrogen as a fuel, which is still limited by a variety of technological hurdles related to the production, handling and storage of hydrogen [1]. The commonly used solution consisting in producing hydrogen by hydrocarbon reforming in a separate system (external reformer) brings more complexity to the experimental set up and limits the overall efficiency of the fuel cell.

Many studies have been devoted to methane, which is the main component of natural gas and biogas [2,3]. Different routes are currently being explored: (i) direct electrochemical oxidation of methane, (ii) a more conventional process including the transient formation of $H_2$ from methane by steam or mixed steam/dry reforming, which can be easily achieved catalytically at the anode due to high temperatures (typically 800–1000 °C). Direct electrochemical oxidation of methane has been more extensively investigated after composite anodes of Cu and $CeO_2$ were shown

to achieve reasonable power densities [4]. Attempts to improve anode performances have been thus carried out [5–9]. On the other hand, the internal steam reforming approach, which attracted most attention in the past years, is still facing two major issues [4,10]. Firstly, carbon deposition due to methane cracking may occur, resulting in a gradual decrease of the electrocatalytic activity and eventually in passageways clogging. This can be observed on Ni/YSZ cermets and an excess of $H_2O$, typically $H_2O/CH_4$ ratios larger than 2, is required, which affects the efficiency of the cell. Secondly, the high endothermicity of the steam reforming reaction combined to the exothermicity of the electrochemical reaction induces strong mechanical constraints at the anode surface, which can cause severe damages in the ceramic components and decrease drastically the lifetime of the fuel cell. A strategy, so called Gradual Internal Reforming (GIR), was proposed to circumvent these problems [11]. Briefly, GIR is based on local coupling between catalytic $CH_4$ steam reforming, which produces hydrogen on specific catalytic sites, and hydrogen electrochemical oxidation, which occurs at the electrode triple-phase perimeter and produces $H_2O$ water vapour. Only very low amounts of water vapour are required at the anode inlet since $H_2O$ is gradually produced along the anode from electrochemical oxidation of $H_2$. In GIR process, heat transfer as exothermic (electrochemical reaction) and endothermic (catalytic reforming) phenomena is better controlled and evenly distributed in the ceramic material since being delocalized along the anode surface. Specific catalytic materials for steam reforming reaction are

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however required because very low $H_2O/CH_4$ ratios, thermodynamically highly favourable to carbon deposition, could be found at the anode surface, at least at the inlet of the anode compartment. A major issue is then to develop catalytic materials highly resistant to carbon deposition [11–13]. The feasibility of using the GIR concept in an intermediate temperature SOFC fed with methane was first demonstrated with a Ru-LaCrO$_3$ anode [11].

Catalytic materials based on ceria as a support were proposed as anode components able to allow GIR conditions for steam and/or dry methane reforming. Ceria did show very interesting properties in various fields of catalysis such as in 3-Way catalytic converters for automotive applications [14], due to their high oxygen storage capacity [15–17]. Interestingly, ceria exhibit some ionic conductivity and doping with alkaline earth or rare-earth metal series results in increased concentration of mobile electronic carriers and improved ionic conductivity [18]. The addition of dopants to pure ceria was also shown to significantly improve its textural (e.g. larger surface area, better porosity) and thermal properties [14,19]. Ceria-based catalysts were shown to catalyze partial oxidation of methane into CO and H$_2$ [20] and steam or dry methane reforming with high resistance against carbon deposition [21]. Very recently, Ir catalysts on Ce$_{0.9}$Gd$_{0.1}$O$_{2-x}$ (CGO) were shown to exhibit high catalytic activity in methane steam reforming under highly water deficient conditions ($H_2O/CH_4 = 0.1$) with only very limited amounts of deposited carbon [22], making these catalysts as good candidates to achieve the catalytic function of a composite anode which would operate under GIR conditions.

The purpose of the present work is to study Gd-doped ceria with the composition Ce$_{0.9}$Gd$_{0.1}$O$_{2-x}$ in methane steam reforming under strongly water deficient conditions ($H_2O/CH_4$ molar ratio of 0.1), in order to better understand the possible role of the CGO support itself in the catalytic reaction over Ir/CGO catalysts when operating under GIR conditions. The catalytic behaviour of Gd-doped ceria in catalytic steam reforming of methane was already reported [21]. However experiments were performed using a $H_2O/CH_4$ molar ratio of 1.1, *i.e.* in conditions strongly different from those used for GIR operation. In particular, we address the influence of thermal treatments of CGO in various atmospheres (N$_2$, H$_2$O or H$_2$) on physicochemical and catalytic properties. We confirm that CGO is weakly active in steam reforming of methane but highly resistant to carbon formation in spite of severe conditions. A moderate deactivation of CGO was also observed with time on stream whenever the sample was pre-exposed to H$_2$-free atmospheres containing atmospheres before reaction. Experimental data strongly suggest this is due to sintering and changes in redox properties, which would be favoured by the presence of H$_2$.

## 2. Experimental

Ce$_{0.9}$Gd$_{0.1}$O$_{2-x}$ with a specific surface area of 44 m$^2$ g$^{-1}$ was supplied by Praxair. CGO was pretreated in various atmospheres at 900 °C: N$_2$, 5% H$_2$O in N$_2$, 5% H$_2$ in N$_2$ (total flow rate of 6.5 L h$^{-1}$). Catalytic activity experiments were carried out in a continuous flow system at atmospheric pressure using a tubular U-shaped quartz reactor. Blank experiments (without CGO samples) were performed showing no H$_2$, CO or CO$_2$ formation. 200 mg of CGO were loaded into the reactor which is mounted inside the furnace. A thermocouple in contact with the external wall of the reactor at the position where the catalyst bed is located allows monitoring the catalyst temperature. The samples were pretreated in N$_2$ (6.5 L h$^{-1}$) at 900 °C for 2 h before catalytic testing. The catalytic activity was investigated at two different molar $H_2O/CH_4$ ratios: 0.1 and 1. In the first case, the reactant mixture consisted of 50 mol% CH$_4$ and 5 mol% H$_2$O with a total flow rate of 6.5 L h$^{-1}$. The molar $H_2O/CH_4$ ratio of 1 was obtained by mixing 5 mol% CH$_4$ and

5 mol% H$_2$O, with a similar total flow rate. N$_2$ was used as the carrier gas. Suitable H$_2$O concentrations were obtained by flowing the adequate mixture of CH$_4$ and N$_2$ dry gases throughout a saturator containing distilled water maintained at 33 °C (thermostated bath). Water content at the reactor outlet was determined using a Edgetech Dew Prime I dew point monitor. Water was trapped with a M&C ECP gas cooler. The reaction products except water vapour were analyzed with a Varian micro-GC equipped with appropriate columns (molecular sieve 5A and Porapak) and thermal conductivity detector (TCD).

Two types of catalytic experiments were carried out. Catalytic tests measurements vs temperature were performed in the range 750–900 °C, starting from 750 °C and increasing temperature by 4 h steps of 50 °C. Isothermal experiments at 900 °C were also carried out for 1, 4 and 24 h. The nature and concentration of the carbonaceous species deposited during isothermal experiments were studied by temperature-programmed oxidation experiments in O$_2$ (O$_2$-TPO) according to the following procedure. After each test, the reactor was purged in N$_2$ at 900 °C, cooled down to room temperature, isolated with 2 valves before being removed from the experimental set up. This allowed preventing sample exposure to air after testing. The reactor was then installed on the O$_2$-TPO experimental set up and purged in He at room temperature. Each sample was then exposed to a 1% O$_2$/He flow (1.8 L h$^{-1}$) at room temperature and O$_2$ adsorption was monitored. After completion of O$_2$ adsorption, the temperature was linearly increased from room temperature to 1000 °C at the rate of 20 °C min$^{-1}$. During adsorption and TPO steps, the gas phase was continuously analyzed using a Pfeiffer Omnistar quadrupole. 1% CO/He and 1% CO$_2$/He mixtures were used for calibration.

Specific surface area was determined by BET nitrogen adsorption using a Micromeritics ASAP2000.

## 3. Results

### 3.1. Catalytic activity measurements

#### 3.1.1. Sample pretreated in nitrogen
Fig. 1 showed the evolution of the products concentrations at the reactor outlet during the catalytic tests over gadolinium-doped ceria (CGO) for $H_2O/CH_4 = 0.1$ at 750, 800, 850 and 900 °C. Up to 800 °C, H$_2$ and CO$_2$ were the only products of the reaction, their concentrations increasing from 750 to 800 °C. At higher temperatures (850 and 900 °C), CO was also observed to form. In this temperature range, CO and H$_2$ concentrations increased with temperature while that of CO$_2$ remained constant. In addition, the
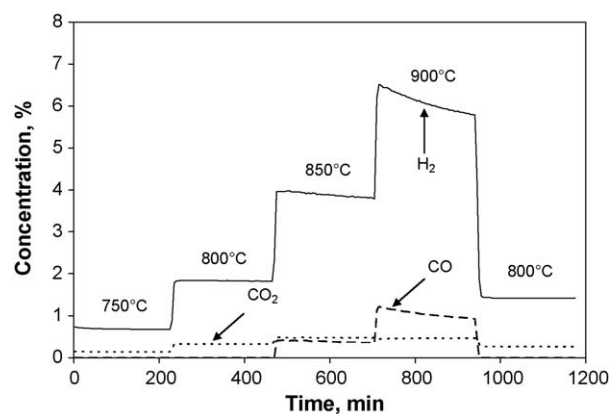


**Fig. 1.** Concentrations of H$_2$ (full line), CO (dashed line), and CO$_2$ (dotted line) as a function of time during the steam reforming of methane over CGO at temperatures between 750 and 900 °C ($H_2O/CH_4 = 0.1$).

**Fig. 2.** Concentrations of $H_2$ (full line), CO (dashed line), and $CO_2$ (dotted line) as a function of time during the steam reforming of methane over CGO at temperatures between 750 and 900 °C ($H_2O/CH_4$ = 1).
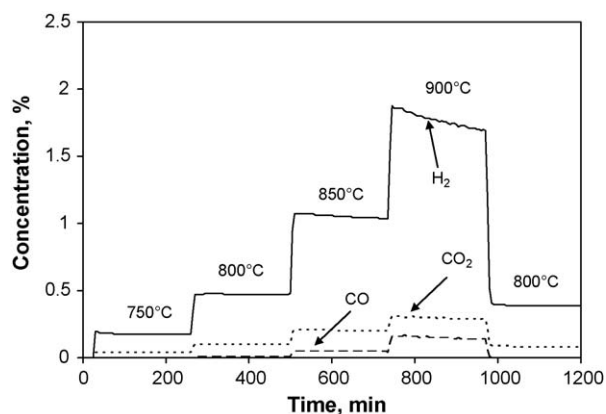


**Fig. 4.** Concentrations of $H_2$ (full line), CO (dashed line), and $CO_2$ (dotted line) as a function of time during the steam reforming of methane over CGO pretreated in $N_2$ at 900 °C during 24 h ($H_2O/CH_4$ = 1).

formation of $H_2$ and CO slightly decreased with time on stream, this behaviour appearing more pronounced at 900 °C. Taking into account the concentration of $H_2O$ was equal to 5 vol.% (limiting reactant), it could be deduced the $H_2$ concentration could not exceed 13.6% (obtained for full conversion of $H_2O$ if considering Steam Reforming reaction). The maximum $H_2$ concentration (7%) was obtained at 900 °C, corresponding to *ca.* 50% conversion of $H_2O$. It decreased gradually to 6.2% after 4 h reaction.

Likewise, for $H_2O/CH_4$ = 1 (Fig. 2), $CO_2$ and $H_2$ were the only products up to 800 °C. Above 800 °C, CO was also produced but in lower amount than $CO_2$. The maximum $H_2$, CO and $CO_2$ concentrations were observed at 900 °C, being respectively equal to 2, 0.17 and 0.3%. As for $H_2O/CH_4$ = 0.1, $H_2$ and, to a lesser extent, CO formations decreased with time on stream, which was clearly observed at 900 °C. In both cases, the catalytic performance at 800 °C was lower after reaction up to 900 °C than before, showing the CGO sample was irreversibly deactivated during reaction at 900 °C. Interestingly, the deactivation was slightly less pronounced for $H_2O/CH_4$ = 1 than for $H_2O/CH_4$ = 0.1.

Isothermal experiments at 900 °C were carried out during 24 h. Figs. 3 and 4 showed the concentrations of the reaction products as a function of time for molar $H_2O/CH_4$ ratios of 0.1 and 1 respectively. For a molar $H_2O/CH_4$ ratio of 0.1, the selectivity to CO decreased with time on stream while the amount of $CO_2$
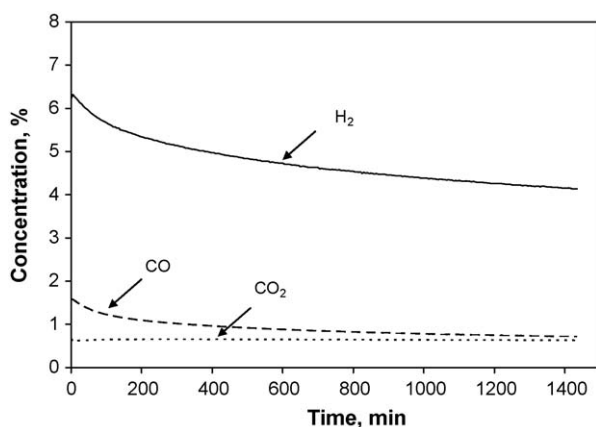
**Table 1**
Hydrogen formation rate vs CGO pretreatment for methane reforming reaction at 900 °C and for $H_2O/CH_4$ = 0.1.

| Catalytic pretreatment gas | Catalytic test duration (h) | Hydrogen formation rate (mmol $g^{-1}$ $s^{-1}$) |
|---|---|---|
| $N_2$ | 1 | 24 |
| $N_2$ | 4 | 20 |
| $N_2$ | 24 | 16 |
| $H_2$ | 4 | 13 |
| $H_2O$ | 4 | 20 |

remained constant. Hydrogen formation rates as a function of time on stream for $H_2O/CH_4$ = 0.1 were given in Table 1.

For a $H_2O/CH_4$ ratio of 1, a similar deactivation trend with time on stream was observed for CO and $H_2$ formation.

### 3.1.2. Sample pretreated in steam-containing $N_2$

Methane reforming was also investigated over fresh sample pretreated in 5% $H_2O/N_2$ flow. Catalytic performance of CGO in steam reforming was measured at 900 °C during 4 h and for a $H_2O/CH_4$ = 0.1 (Fig. 5). The same catalytic behaviour of CGO as that obtained after nitrogen pre-treatment could be observed. $H_2$, CO and $CO_2$ were formed. As for the sample pretreated in $N_2$, CO and $H_2$ concentrations decreased with time on stream (from 7 to 5.7%
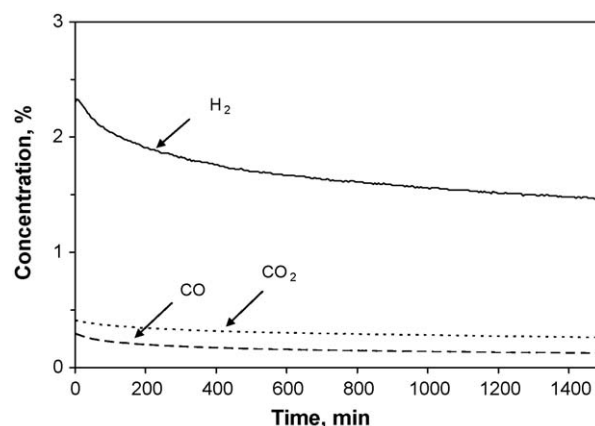


**Fig. 3.** Concentrations of $H_2$ (full line), CO (dashed line), and $CO_2$ (dotted line) as a function of time during the steam reforming of methane over CGO pretreated under $N_2$ and tested at 900 °C during 24 h ($H_2O/CH_4$ = 0.1).



**Fig. 5.** Concentrations of $H_2$ (full line), CO (dashed line), and $CO_2$ (dotted line) as a function of time during the steam reforming of methane over CGO preactivated in 5% $H_2O/N_2$ and tested at 900 °C during 24 h ($H_2O/CH_4$ = 0.1).
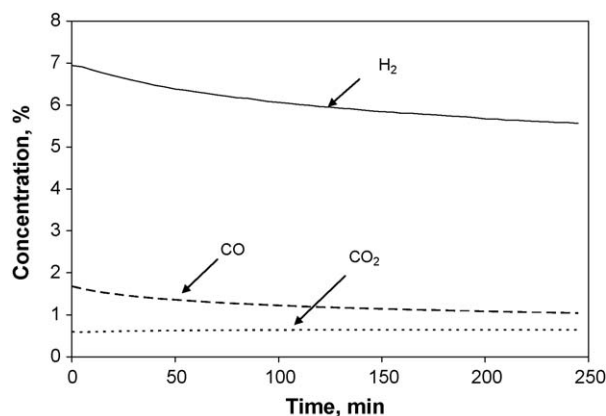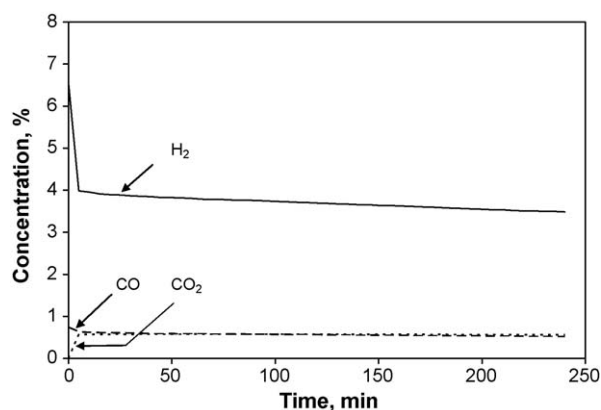
**Fig. 6.** Concentrations of $H_2$ (full line), CO (dashed line), and $CO_2$ (dotted line) as a function of time during the steam reforming of methane over CGO pretreated in 5% $H_2/N_2$ and tested at 900 °C during 24 h ($H_2O/CH_4 = 0.1$).

**Table 2**
Specific surface areas of CGO samples measured before and after reaction.

| Pretreatment | Catalytic test duration | Surface area ($m^2 g^{-1}$) | Average crystallite size (nm) |
|---|---|---|---|
| no (fresh CGO) | – | 44 | 28 |
| $N_2$ | | | |
| 2 h | – | $9 \pm 0.5^a$ | 91 |
| 19 h | – | $9 \pm 0.5^a$ | |
| $H_2O$ | | | |
| 2 h | – | 9 | 65 |
| $H_2$ | | | |
| 2 h | – | 2 | 195 |
| 16 h | – | 3 | |
| $N_2$ | | | |
| 2 h | 1 h | 3 | 108 |
| 2 h | 24 h | $3.5 \pm 0.5^a$ | |
| $H_2$ | | | |
| 16 h | 24 h | 1.5 | |

<sup>a</sup> Average value calculated from 2 measurements.

for $H_2$ and from 1.7 to 1% for CO), the $CO_2$ concentration remaining constant and equal to 0.7%.

### 3.1.3. Sample pretreated in $H_2$-containing $N_2$

Fig. 6 showed catalytic data of $CH_4$ reforming reactions performed at 900 °C ($H_2O/CH_4 = 0.1$) over the CGO sample previously activated in 5% $H_2/N_2$ for 2 h at 900 °C. The profile observed was different from those recorded with samples pretreated in $N_2$ or $H_2O$. During the first minutes of catalytic test, a sharp peak of $H_2$ production (6.7%) was observed while 0.8% CO was detected and no $CO_2$ produced. A rapid reaction between $H_2O$ and reduced CGO sites (likely $Ce^{3+}$ formed during $H_2$ pretreatment) according to Eq. (1) was proposed to explain the initial production of hydrogen:

$$nH_2O + CeO_{2-n} \rightarrow nH_2 + CeO_2 \qquad (1)$$

Once CGO reduced surface sites have been re-oxidised by $H_2O$, $H_2$, $CO_2$ and CO were formed simultaneously and only a little variation of concentration was observed with reaction time. It could be noted that the pretreatment in $H_2$ led to a lower activity (ca. 3.8% $H_2$ after 4 h reaction) compared to pretreatments in $N_2$ or $H_2O/N_2$ (ca. 6% $H_2$ after 4 h reaction).

### 3.2. Characterization results

#### 3.2.1. BET surface area

The specific surface area of the CGO samples pretreated in various atmospheres was measured after various times on stream (reforming reaction). The values together with the corresponding average crystallite sizes were summarized in Table 2. For all samples, the BET surface area dramatically decreased from 44 to 9 and 2 $m^2 g^{-1}$ upon pretreatment at 900 °C in $N_2$ (or $H_2O/N_2$) and $H_2$ respectively. It could be also noted that, for the sample pretreated in $N_2$, a further decrease of surface area (from 9 to 3 $m^2 g^{-1}$) occurred upon sample exposure to reaction mixture.

#### 3.2.2. Oxygen adsorption and TPO experiments after catalytic testing

Samples pretreated in $N_2$, $H_2O/N_2$ or $H_2/N_2$ at 900 °C and submitted to the reaction mixture with $H_2O/CH_4 = 0.1$ at 900 °C were exposed (without contact to air) at room temperature to a 1 vol% $O_2$/He flow. This caused the consumption of oxygen during a few minutes, which could be attributed to catalyst re-oxidation. The results were reported in Table 3.

Re-oxidation at room temperature strongly depended on the pretreatment atmosphere. Upon pretreatment in $H_2O/N_2$, no $O_2$ adsorption occurred, likely indicating the full oxidation of the CGO sample. On the contrary, the $H_2$ treatment led to an expected deep partial reduction of CGO, at least partially re-oxidised upon $O_2$ adsorption at room temperature (748 $\mu mol$ $O_2$ $g^{-1}$). After $N_2$ treatment, the consumption of 32 $\mu mol$ $O_2$ $g^{-1}$ of catalyst would indicate that the treatment in inert gas surprisingly led to a slight CGO reduction. Obviously, it could not be stated from these experiments that the re-oxidation of reduced species formed during treatment in $H_2$ and, to a lower extent, $N_2$ was completed.

The influence of the reaction duration over samples pretreated in $N_2$ at 900 °C was also addressed. After 1 h reaction, the amount of $O_2$ consumed at room temperature sharply increased up to 117 $\mu mol$ (g catalyst)$^{-1}$ with respect to that after $N_2$-pretreatment alone (32 $\mu mol$ $O_2$ $g^{-1}$). This could be attributed to a further extent of CGO reduction under reaction mixture, which was expected if considering the strongly reducing character of the reaction mixture compared to inert gas. Increasing time on stream induced a slight decrease of the amount of $O_2$ consumed for re-oxidation.

After 4 h reaction following pretreatments in $H_2O/N_2$ and $N_2$, similar amounts of $O_2$ were consumed at room temperature (110 and 95 $\mu mol$ $g^{-1}$ respectively). The reducing character of the reaction mixture with respect to $N_2$ or $H_2O/N_2$ would explain again the partial reduction of CGO. More surprising was the result obtained upon 4 h reaction after $H_2$ treatment. The amount of consumed $O_2$ appeared abnormally small (54 $\mu mol$ $g^{-1}$) compared to that after $H_2$ pretreatment only (748 $\mu mol$ $g^{-1}$) if considering the reducing capability of both $H_2$ and reaction mixture. It could be inferred that, irrespective of the pretreatment and in spite of the large excess of $CH_4$ with respect to $H_2O$, CGO is only partially reduced in the reaction mixture.

During these adsorption experiments, small amounts of $CO_2$ are always observed to adsorb with $O_2$, likely as weakly bonded carbonate species. This is due to the presence of $CO_2$ traces in the oxygen/He mixture. $CO_2$ adsorption is also reported in Table 3. $CO_2$ adsorption in $O_2$ containing atmosphere is likely made possible due to the re-formation of oxidised CGO surface sites with basic character or to oxidised surface sites still existing after pretreatment in $N_2$ or reaction. The amount of adsorbed $CO_2$ is small

**Table 3**
Oxygen consumption and $CO_2$ formation ($\mu$mol g$^{-1}$) during $O_2$ adsorption[a] and TPO experiment[b] after pretreatment with various atmospheres[c] and reaction[d] over CGO samples.

| Pretreatment | Time on stream | $O_2$ adsorption | | TPO experiment | | | |
|---|---|---|---|---|---|---|---|
| | | | | Processes between 25 and 400 °C | | Processes above 600 °C | |
| | | $O_2$ ads | $CO_2$ ads | $O_2$ consumed | $CO_2$ formed | $O_2$ consumed | $CO_2$ formed |
| $N_2$ | | | | | | | |
| 2 h | –[c] | 32 | 8 | – | 8 | 4 | 4 |
| $H_2O$ | | | | | | | |
| 2 h | –[c] | 0 | 20 | 3 | 20 | – | 1 |
| $H_2$ | | | | | | | |
| 2 h | –[c] | 748 | 6 | 3 | 3 | – | 2.5 |
| $N_2$ | | | | | | | |
| 2 h | 1 h | 117 | 6 | 10 | 6 | – | 4 |
| 2 h | 4 h | 95 | 6 | 8 | 5 | 3 | 5 |
| 2 h | 24 h | 80 | 3 | 11 | 3.5 | 21 | 20 |
| $H_2O$ | | | | | | | |
| 2 h | 4 h | 110 | 6.5 | 10 | 6.5 | – | 0 |
| $H_2$ | | | | | | | |
| 2 h | 4 h | 54 | 2 | 17 | 2 | – | 13 |

[a] Samples were exposed to 1% $O_2$/He flow at room temperature.
[b] Samples were exposed to 1% $O_2$/He from room temperature to 1000 °C (20 °C min$^{-1}$).
[c] Samples have been submitted to pretreatment only at 900 °C.
[d] Samples have been pretreated and tested in reaction at 900 °C ($H_2O$/$CH_4$ = 0.1).

(typically $\leq 8$ $\mu$mol/g). The larger value obtained for the sample treated in $H_2O$/$N_2$ (20 $\mu$mol g$^{-1}$) could be related to a higher oxidation extent of the surface (no $O_2$ adsorption).

TPO experiments were carried out after $O_2$ consumption. As an example, Fig. 7 showed the $O_2$ consumption and $CO_2$ formation profiles obtained from $O_2$-TPO experiment over $N_2$-pretreated CGO after 24 h reforming reaction at 900 °C ($H_2O$/$CH_4$ = 0.1). Two different temperature ranges could be distinguished, namely low temperature (25–400 °C) and high temperature (600–1000 °C). The $O_2$ consumption peak at 130 °C could be associated with re-oxidation of surface sites, which confirmed that the RT $O_2$ re-oxidation was not complete. Again it could not be stated that the CGO sample was fully re-oxidised at this stage. A small peak of $CO_2$ desorption could be detected in this range of temperature, which might be explained by the decomposition of weakly bonded carbonates formed upon $O_2$ adsorption step (see Table 3). Above 600 °C, a perfect accordance between consumed $O_2$ and released $CO_2$ profiles was observed. This could be attributed to the total oxidation of carbon-containing species (coke) deposited on the



**Fig. 7.** Oxygen consumption (full line) and $CO_2$ formation (dashed line) rates during $O_2$-TPO experiment over CGO sample pretreated in $N_2$ and tested in methane reforming at 900 °C for 24 h ($H_2O$/$CH_4$ = 0.1).

sample during reaction. It must be pointed out that amounts were very small. The coke formation was highly suggested a slight change of colour turning from beige to light grey. The formation of carbon-containing residues over oxide catalysts could be explained by gas-phase mechanisms on the contrary to catalysis on metals (e.g. Ni) at high temperatures, which involves $CH_4$ cracking at the metal surface. $CO_2$ release could be the decomposition of highly stable carbonate species on reduced ceria surface sites upon high temperature re-oxidation. This alternative explanation, although it could not be totally ruled out, seems less likely possible. Carbonates stabilized in reduced atmosphere were reported to decompose around 500 °C in oxidising atmosphere [23,24]. However, the phenomenon we observed in the present work took place around 800 °C, i.e. at much higher temperatures than already reported. In addition, the strict correspondence between $O_2$ consumption and $CO_2$ formation would imply the only presence of bidentate species on two adjacent cerium sites.

Table 3 summarized the amounts of consumed $O_2$ and released $CO_2$ during TPO in low temperature range (25–400 °C) and high temperature range (600–1000 °C) for different samples. The results for the fresh sample activated under nitrogen flow during 2 h are also included.

In the low temperature range, irrespective of the sample, the amount of released $CO_2$ fitted exactly the amount of $CO_2$ adsorbed at room temperature. This confirmed the adsorption of $CO_2$ traces during the $O_2$/He adsorption step as carbonates weakly bonded to oxidised sites. Simultaneously, oxygen adsorbed, indicating that CGO samples were only partially re-oxidised at room temperature in $O_2$/He. The proportion of the low temperature $O_2$ consumption with respect to RT adsorption strongly depended on the history of the sample, being negligible for samples pretreated in $N_2$ or $H_2O$/$N_2$ and contacted with reforming mixture while being comparable for the $H_2$-treated sample.

In the high temperature range, no $CO_2$ was released for the $H_2O$-pretreated sample being or not exposed to reaction mixture. It could be inferred that $H_2O$ treatment prevented the formation of carbon deposits. For other samples, the amount of consumed oxygen exactly fitted the amount of released $CO_2$ in agreement
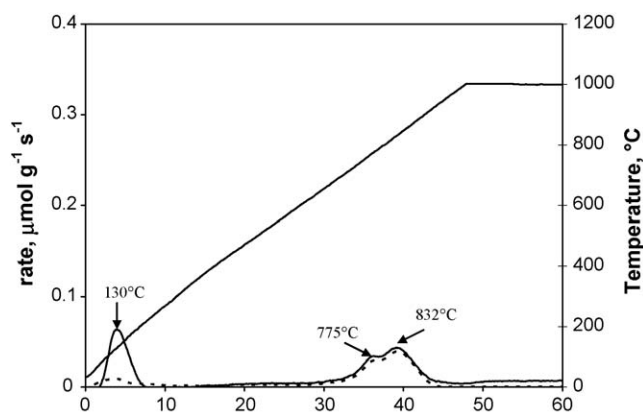
with the complete oxidation of carbon deposits as discussed above. Only very small amounts of $CO_2$ were measured in all cases, showing the remarkably high resistance of CGO to carbon deposition in conditions strongly thermodynamically favourable to its formation. CGO appears comparable to pure ceria to this respect [21]. Variations between samples were very small and might be not significant.

## 4. Discussion

The reaction conducted between $CH_4$ and $H_2O$ leads to the formation of hydrogen, CO and $CO_2$ as main products, a little amount of carbon is also produced when the catalyst is pretreated under nitrogen or hydrogen. The reactions explaining the formation of such products are described as follows:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (2)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 2H_2 \qquad (4)$$

$$2CO \rightleftarrows C + CO_2 \qquad (5)$$

$$CH_4 \rightleftarrows C + 2H_2 \qquad (6)$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad (7)$$

Below 800 °C, only $CO_2$ and $H_2$ are detected, which is possibly explained by the water gas shift equilibrium (WGS, Eq. (3)), being shifted toward $CO_2$ formation, in addition to the steam reforming reaction (Reaction (2)). Above 825 °C, WGS equilibrium is then shifted to the CO production. CO and $CO_2$ can conjointly form along with hydrogen produced through Reaction (2). It can be inferred that Reactions (2) and (4) are kinetically limited while Reaction (3) is very fast at such high temperatures, being under thermodynamic control. As a matter of fact, Reaction (4) can be considered as the result of Reactions (2) and (3). However, it cannot be excluded that Reaction (4) takes place under kinetic limitations over specific active sites. These sites would be not affected during catalytic testing on the contrary to sites responsible for steam reforming (Reaction (2)). This would explain the surprising unchanged production of $CO_2$.

Increasing the $H_2O/CH_4$ ratio from 0.1 to 1 leads qualitatively to the same reactions above described while product distribution changes, giving more $CO_2$ than CO in agreement with the increase in water molar fraction, which favours both Reactions (3) and (4). CO might also be converted into carbon and $CO_2$ through Boudouart reaction (Eq. (5)). The carbon formation might also result from the cracking of methane (Eq. (6)). Taking into account the large excess of methane ($H_2O/CH_4 = 0.1$) the feasibility of dry reforming reaction (Eq. (7)) cannot be ruled out.

A redox mechanism is now commonly admitted for explaining the steam reforming reaction over ceria [25]. The first step would involve the partial reduction of ceria by methane according to the Reaction (8):

$$CeO_2 + nCH_4 \rightarrow CeO_{2-n} + nCO + 2nH_2 \qquad (8)$$
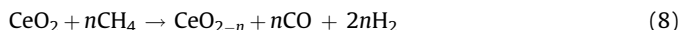
The second step would be the re-oxidation of ceria by $H_2O$ according to Reaction (9):

$$CeO_{2-n} + nH_2O \rightarrow CeO_2 + nH_2 \qquad (9)$$

The same mechanism can apply to the ceria fraction in CGO solid solution.

It is observed in our experiments that CGO activity for methane steam reforming decreases with increasing time on stream in most
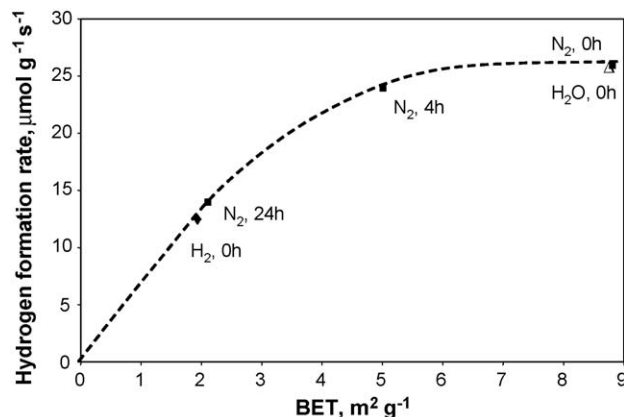


**Fig. 8.** Hydrogen formation rate as a function of the specific surface area measured after using CGO samples in methane reforming at 900 °C ($H_2O/CH_4 = 0.1$).

operating conditions except for the hydrogen pretreated samples. This suggests that hydrogen plays somehow a role in the deactivation process, which will be addressed later on in the discussion. Deactivation induced by pretreatments and occurring during reaction might be explained in three ways: (i) surface area changes as a result of CGO sintering during pretreatment and reaction; (ii) carbon deposition as a side reaction of methane reforming leading to possible active site inaccessibility and (iii) blockage of the redox mechanism by stabilization of reduced sites.

Concerning the first explanation, a complex relationship between the catalytic behaviour in methane steam reforming and the surface area is observed (Fig. 8). For surface area larger than 6 $m^2 g^{-1}$ the activity is independent on surface area, while below this value, the CGO surface area has some effect, being more important as sintering increases. Changes in the activity shown for samples with smaller surface areas are probably coupled with a loss in the ability of ceria to transfer oxygen when treated in severe conditions [26,17]. It can be concluded that the observed sintering is at least partly responsible for catalyst deactivation.

The second explanation for CGO deactivation in steam reforming of methane concerns the carbon deposit formation. The concentration of carbonaceous species deposited on the sample (determined by TPO) slightly varies when changing pretreatment, time on stream or $H_2O/CH_4$ ratio. Carbon formation which is always limited in our experiments does not seem playing a crucial role in deactivation mechanism. In order to prove this statement, we studied the influence of a purge in $O_2$ after catalytic test (Fig. 9). The $N_2$-pretreated sample was exposed to the reaction mixture for 24 h before being treated in 5% oxygen/$N_2$ flow during 30 min. The activity was only slightly restored together with the transient release of $CO_2$. $CO_2$ formation is explained by oxidation of carbon deposit formed during reaction. It is clear that this deposit has a little influence on catalytic activity, considering the very small regeneration observed. This effect, although very limited, exists since a purge in $N_2$ does not affect catalytic activity at all.

The third possibility which should be considered for explaining deactivation consists the blockage of the redox mechanism (Eqs. (8) and (9)). It can be stated that CGO is only partially reduced upon reaction: reduction of some $Ce^{4+}$ sites into $Ce^{3+}$. $Ce^{3+}$ content in the used catalyst with respect to $Ce^{4+}$ in the fresh catalyst should be at least equal to that derived from $O_2$ consumption upon re-oxidation. Let us note that the reduction percentage of $Ce^{4+}$ in CGO after reaction from oxygen consumption below 200 °C never exceeds 2%, which is low considering the strongly reducing atmosphere of the catalytic testing. This is consistent however with the observation of low carbon formation
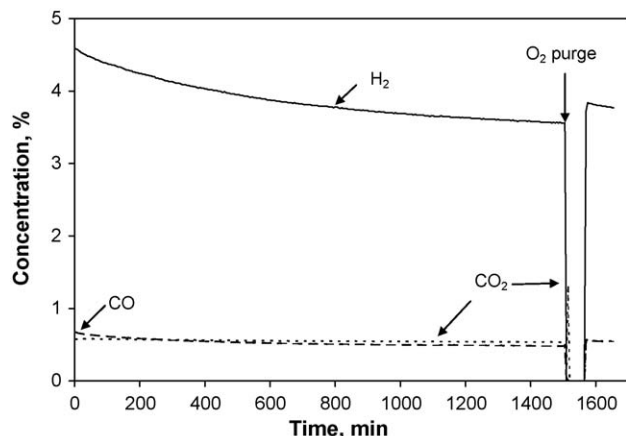
**Fig. 9.** Effect of a purge in 5% $O_2/N_2$ on the activity of CGO after 24 h reaction ($H_2O/CH_4 = 0.1$) at 900 °C.

as indicated by Otsuka et al. [20,27], showing almost no carbon deposit if the degree of reduction remains lower than 10%.

A more extensive reduction (12%) is only observed upon pretreatment in hydrogen without subsequent reaction. Based on the paper by Zalc et al. studying Pd/ceria catalysts in WGS reaction at 400–500 °C [28], the complete re-oxidation of ceria cannot be achieved after reduction of ceria in $H_2$ atmosphere. The authors proposed that hydrogen treatment leads to an irreversible overreduction of ceria. In our case, the sample pretreated in hydrogen and used in reaction leads to the smallest number of re-oxidised species. An irreversible effect of hydrogen on CGO in our experiments after $H_2$-pretreatment should take place as invoked by Zalc et al. Ce(III)(OH)$_2$ species are proposed to be produced upon reaction of hydrogen with oxidised species. These species are possibly highly stable, inhibiting re-oxidation process and therefore affecting the number of re-oxidised species. For $N_2$- or $H_2O$-pretreated samples, the progressive deactivation can be tentatively attributed to hydrogen produced during the reaction leading to the formation of irreversibly reduced species.

The role of surface oxidised species of doped or undoped ceria in catalytic processes was discussed by Chadwick et al. [29] and Gorte et al. [16,17]. In our experiment, the number of reduced species formed during the reaction and re-oxidised by $O_2$ (below 200 °C) varies linearly with catalytic activity (Fig. 10). These species could
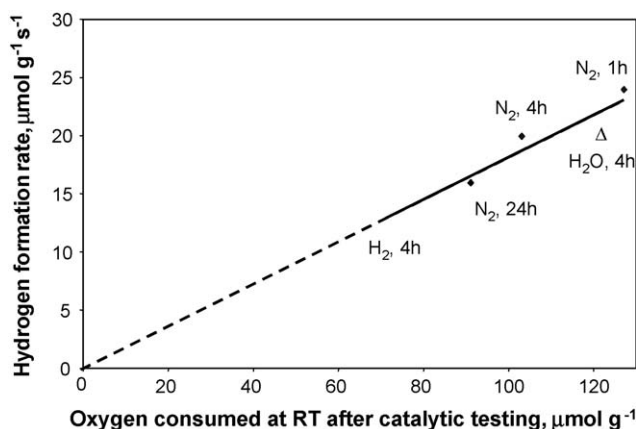
be tentatively attributed to the active sites. Based on our results, the number of such species seems to depend on the surface area and mainly on the presence of hydrogen in pretreatment or reaction gas phase.

## 5. Conclusions

Gd-doped ceria exhibits a measurable catalytic activity performance for methane reforming reaction in strongly water deficient conditions. Structural and catalytic properties of CGO depend on the pretreatment procedure. The sample pretreated with $H_2O$ exhibits exactly the same activity and the same slow deactivation as the sample activated in nitrogen. The sample pretreated with hydrogen is less active and, interestingly, does not deactivate. The observed decrease of CGO surface area upon thermal pretreatment and/or catalytic testing is thought to only have a partial effect on reaction rate. Carbon deposits always form in limited amounts although a large excess of methane is used with respect to $H_2O$. No evidence for carbon deposits being significantly responsible for deactivation can be established.

Irreversible changes in the redox properties of catalyst taking place during reaction or upon $H_2$ treatment are clearly evidenced. The formation of highly stable irreversibly reduced species in $H_2$-containing atmosphere (pretreatment or reaction mixture) is thought to be responsible for CGO deactivation.

**Fig. 10.** Hydrogen formation rate as a function of oxygen consumed at room temperature over CGO samples after methane reforming at 900 °C ($H_2O/CH_4 = 0.1$). Different symbols indicate the use of different pretreatments.

## References

[1] R.F. Service, Science 285 (1999) 682–685.
[2] M. Hammad, D. Badarneh, K. Tahboub, Energy Convers. Manage. 40 (1999) 1463.
[3] Y. Shiratori, T. Oshima, K. Sasaki, Int. J. Hydrogen Energy 33 (2008) 6316.
[4] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. McEvoy, M.B. Mogensen, S. Singhal, J. Vohs, Nat. Mater. 3 (2004) 17.
[5] B.C.H. Steele, P.H. Middleton, R. Rudkin, Solid State Ionics 40/41 (1990) 388.
[6] S. Putna, J. Stubenrauch, J.M. Vohs, R.J. Gorte, Langmuir 11 (1995) 4832.
[7] M.D. Gross, J.M. Vohs, R.J. Gorte, Electrochem. Solid State Lett. 10 (2007) B65–69.
[8] G. Kim, J.M. Vohs, R.J. Gorte, J. Mater. Chem. 18 (2008) 2386.
[9] G. Kim, G. Gorre, J.T.S. Irvine, J.M. Vohs, R.J. Gorte, Electrochem. Solid State Lett. 11 (2008) B16–19.
[10] J. Sfeir, J. Van Herle, J.A. McEvoy, in: Proceedings of 3rd European Solid Oxide Fuel Cell Forum, 1998, p. 267.
[11] P. Vernoux, J. Guindet, M. Kleitz, J. Electrochem. Soc. 145 (1998) 3487.
[12] E. Puzenat, P. Gélin, 7th European Congress on Catalysis EUROPACAT-VII, Sofia, Bulgaria, August 20–September 1, 2005.
[13] M. Wisniewski, A. Boréave, P. Gélin, Catal. Commun. 6 (2005) 596.
[14] A. Trovarelli, in: A. Trovarelli (Ed.), Catalysis by Ceria and Related Materials, Catalysis Sciences Series, vol. 2, Imperial College Press, 2002, pp. 15–50.
[15] H. Cordatos, T. Bunluesin, J. Stubenrauch, J.M. Vohs, R.J. Gorte, J. Phys. Chem. 100 (1996) 785.
[16] T. Bunluesin, R.J. Gorte, G.W. Graham, Appl. Catal. B 14 (1997) 105.
[17] T. Bunluesin, R.J. Gorte, G.W. Graham, Appl. Catal. B 15 (1998) 107.
[18] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1.
[19] H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.P. Cuif, S.E. Deutsh, O. Touret, Catal. Today 50 (1999) 309.
[20] K. Otsuka, Y. Wang, E. Sunada, I. Yamanaka, J. Catal. 175 (1998) 152.
[21] E. Ramirez-Cabrera, A. Atkinson, D. Chadwick, Appl. Catal. B 36 (2002) 193.
[22] J. Toyir, H. Belatel, A. Kaddouri, P. Gélin, in preparation.
[23] S. Sharma, S. Hilaire, J.M. Vohs, R.J. Gorte, H.-W. Jen, J. Catal. 190 (2000) 199.
[24] S. Hilaire, X. Wang, T. Luo, R.J. Gorte, J. Wagner, Appl. Catal. A 215 (2001) 271.
[25] K. Otsuka, T. Ushiyama, I. Yamanaka, Chem. Lett. (1993) 1517.
[26] M. Zalc, V. Sokolovskii, D.G. Loffler, J. Catal. 206 (2002) 169.
[27] K. Otsuka, E. Sunada, T. Ushiyama, I. Yamanaka, Stud. Surf. Sci. Catal. 107 (1997) 531.
[28] J.M. Zalc, V. Sokolovskii, D.G. Loffler, J. Catal. 206 (2002) 169.
[29] E. Ramirez-Cabrera, A. Atkinson, D. Chadwik, Appl. Catal. B 47 (2004) 127.